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U. S. DEPARTMENT OF AGRICULTURE,

BUREAU OF CHEMISTRY—BULLETIN No. 153.

R. E. DOOLITTLE, ACTING CHIEF OF BUREAU.

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# DETERMINATION OF LITHIUM.

BY

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*Chief, Water Laboratory,*

AND

W. D. COLLINS,  
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PREPARED UNDER THE DIRECTION OF

J. K. HAYWOOD,  
*Chief, Miscellaneous Division.*



WASHINGTON:  
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## LETTER OF TRANSMITTAL.

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U. S. DEPARTMENT OF AGRICULTURE,  
BUREAU OF CHEMISTRY,  
*Washington, D. C., April 8, 1912.*

SIR: I have the honor to transmit for your inspection and approval a manuscript prepared in the Miscellaneous Division of the Bureau of Chemistry, reporting results of an investigation of methods for the determination of lithium and a spectroscopic method developed in this bureau for the determination of small amounts of this element. I recommend that this manuscript be published as Bulletin No. 153 of the Bureau of Chemistry.

Respectfully,

R. E. DOOLITTLE,  
*Acting Chief of Bureau.*

Hon. JAMES WILSON,  
*Secretary of Agriculture.*

## LETTER OF SUBMITTAL.

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U. S. DEPARTMENT OF AGRICULTURE,  
BUREAU OF CHEMISTRY,  
*Washington, D. C., March 20, 1912.*

SIR: I have the honor to submit for your inspection and approval a manuscript giving the results of an investigation of methods for the determination of lithium, prepared by W. W. Skinner, Chief, and W. D. Collins, First Assistant Chemist, of the Water Laboratory of the Miscellaneous Division.

In the enforcement of the food and drugs act it was found necessary to study carefully methods for the determination of small amounts of lithium, such as exist in most mineral waters, some soft drinks, etc. As a result of this study the authors have perfected a quantitative spectroscopic method for this purpose which is of great value in the work we are doing. This method has been given a thorough test extending over a period of two years and has been adopted as a part of our regular technique in mineral-water analyses. The manuscript transmitted herewith gives the method developed by Messrs. Skinner and Collins, together with a comprehensive review of the literature of the subject of the determination of lithium, and makes a valuable addition to the technical papers prepared in this bureau. I recommend that the report be published as a bulletin of this bureau.

Respectfully,

J. K. HAYWOOD,  
*Chief Miscellaneous Division.*

R. E. DOOLITTLE,  
*Acting Chief Bureau of Chemistry.*

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# THE DETERMINATION OF LITHIUM.

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## INTRODUCTION.

In the examination of mineral waters for lithium there is need of a method by which small amounts of this substance may be determined with reasonable accuracy when only relatively small amounts (from 1 to 5 liters) of water are available for this determination in the general scheme of a complete mineral water analysis. Where the amount of lithium present is as small as 0.001 mg per liter, the evaporation of a quantity of water large enough to give a weighable quantity of lithium salt consumes so much time and gives such large quantities of other salts that it seems better to use a small quantity of water and determine the lithium spectroscopically after it is separated from the other constituents.

In such cases the separation from the other substances in the water is carried out according to the provisional method of the Association of Official Agricultural Chemists<sup>1</sup> first proposed by Gooch,<sup>2</sup> which is regularly used in the water laboratory of the Bureau of Chemistry when weighable quantities of lithium are present. The spectroscopic determination is made on a solution of the sulphates of lithium, sodium, and potassium obtained by the Gooch method of separation with amyl alcohol. A preliminary paper by one of the authors<sup>3</sup> read at the thirty-ninth annual meeting of the American Association for the Advancement of Science, at Baltimore, 1908, gave a brief outline and review of the work, making use of the spectroscope in the quantitative determination of lithium and the effect of the masking of the red lithium line ( $\text{Li}_\alpha$ ) by various amounts of sodium and potassium. In this bulletin is given a review of methods which have been considered or tested for the separation of lithium and a method developed by the authors for the determination by the spectroscope of the small amount of lithium usually found in mineral waters and in some other substances.

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<sup>1</sup> U. S. Dept. Agr., Bureau of Chemistry Cir. 52.

<sup>2</sup> Amer. Chem. J., 1887, 9: 33-51.

<sup>3</sup> Skinner. A spectroscopic method for the determination of lithium.

## QUANTITATIVE SEPARATION OF LITHIUM.

## REVIEW OF METHODS DESCRIBED IN THE LITERATURE.

Before the appearance of Gooch's article in 1887, the method most used by chemists was that of Berzelius<sup>1</sup> modified by Mayer.<sup>2</sup> Berzelius added phosphoric acid and sodium carbonate to the mixed alkali chlorids and evaporated to dryness. On taking up with cold water, a white powder was left behind which was insoluble in the sodium phosphate mother liquor and could be washed with cold water. This precipitate he considered a double phosphate of sodium and lithium with equivalent amounts of each metal. One analysis of a precipitate showed very nearly this relation.

RAMMELSBERG<sup>3</sup> found that the filtrates and wash waters from the phosphate precipitate of Berzelius contained lithium on account of the solubility of the lithium phosphate. He also found the sodium to vary from 7.845 to 28.38 per cent and the lithium from 34.36 to 21.89 per cent according to the variations in the amounts of sodium and lithium in the solution from which the precipitate was formed. He concluded therefore that the phosphate separation was unreliable and suggested the use of ether and alcohol to make a quantitative separation. He extracted the dried mixed chlorids with a mixture of equal parts of ether and absolute alcohol. This solvent dissolved the lithium chlorid and left the sodium and potassium chlorids. After evaporation of the solvent, the lithium could be converted into sulphate for weighing. In a further study<sup>4</sup> of the phosphates of lithium he found varying proportions of lithium oxid and phosphoric acid with different methods of formation of the precipitate.

J. LAWRENCE SMITH,<sup>5</sup> writing on the determination of the alkalis, gave the method of Rammelsberg as affording a satisfactory separation and reported some results which do not show as clean separation as might be desired. While the results are not very clearly expressed, the calculation by Gooch<sup>6</sup> seems to be the only one that will show just what quantities of lithium were used and recovered. According to these figures, Smith, by treating 0.5 gram of potassium chlorid with 10 grams of ether-alcohol mixture dissolved 0.0003 gram of the salt and from 0.5 gram of sodium chlorid dissolved 0.0005 gram with the same amount of ether-alcohol, giving a total weight of 0.0008 gram dissolved from the two salts. From a mixture of 0.2 gram each of potassium chlorid and sodium chlorid and 0.0080 gram of lithium chlorid, he recovered 0.0101 gram, presumably lithium chlorid, an excess of 0.0021 gram. From a "similar mixture," supposedly 0.2 gram each of potassium chlorid and sodium chlorid, with 18.1 per

<sup>1</sup> Pogg. Ann., 1825 4: 245.

<sup>2</sup> Ann. Chem. Pharm., 1856, 98: 193.

<sup>3</sup> Pogg. Ann., 1845, 66: 79.

<sup>4</sup> Pogg. Ann., 1849, 76: 261-270.

<sup>5</sup> Amer. J. Sci., 1853 (2) 16: 56.

<sup>6</sup> Loc. cit.

cent, or 0.0885 gram, of lithium chlorid, he recovered 17.65 per cent, or 0.0862 gram, a deficiency of 0.0023 gram of lithium chlorid. Again from a similar mixture containing 67.2 per cent or 0.8200 gram of lithium chlorid, he recovered 68.4 per cent, or 0.8340 gram, equivalent to an excess of 0.0140 gram of lithium chlorid. While in judging most methods, it is fairer to rate the results by the percentage of the substance sought which is recovered, in the case of a determination with constant sources of error, such as the increased solubility of the sodium and potassium chlorids due to moisture in the ether-alcohol and the failure to obtain complete extraction of small amounts of lithium from large amounts of the other chlorids, the value of the method for determining small amounts depends upon the absolute amount of error. From this point of view, Smith's errors of 0.0140 gram, 0.0023 gram and 0.0021 gram of lithium chlorid show the method to be very poorly suited to the determination of lithium in natural waters which very rarely contain more than 0.01 gram per liter.

MAYER<sup>1</sup> noted that Liebig had found a carbonate left in the precipitate formed by the use of phosphoric acid and sodium carbonate. In view of the work of Rammelsberg and the fact that the phosphate method was in such general use, Mayer made a study of the precipitation under different conditions. He obtained only pure lithium phosphate ( $\text{Li}_3\text{PO}_4$ ) by evaporating to dryness with sodium phosphate and enough sodium hydroxid to render the liquid alkaline. If sodium carbonate were used in neutralizing the liquid, some carbonate was found in the precipitate. He found it difficult to wash out the last traces of sodium from large precipitates, but by thorough washing was always able to obtain a residue free from sodium and consisting of tri-basic lithium phosphate ( $\text{Li}_3\text{PO}_4$ ). He claimed that the three lithium phosphates of Rammelsberg were the same with varying amounts of water. The thorough washing required by Mayer dissolved so much lithium that he found it necessary to evaporate the filtrate and wash water and take up with water and wash the precipitate. With careful work he obtained only about 1.5 per cent of the total lithium precipitate in the second separation. He washed with equal volumes of water and ammonia, and noted that in the presence of relatively large amounts of sodium and potassium salts, the greater part of these must be removed before separating the lithium as phosphate, as the amount of water necessary to wash out the alkali salts would dissolve too much lithium. He dissolved 0.110 gram of sodium chlorid in 100 grams of a mixture of 96 per cent alcohol and 98 per cent ether, and noted that in tests made by Rammelsberg 1.33 per cent of the sodium chlorid used went into solution with the lithium chlorid. He also observed the tendency

<sup>1</sup> Ann. Chem. Pharm., 1856, 98: 193.

of lithium chlorid to decompose on drying, forming hydroxid, which, he said, was not soluble in ether-alcohol. The tri-basic phosphate is soluble one part in 2539 parts of cold water and in 3920 parts of water and ammonia. In ammonium chlorid solution the precipitate was very soluble.

Mayer stated that Rammelsberg obtained from 100 parts of lithium chlorid from 143.6 to 89 parts of mixed phosphate. The higher results he attributed to the sodium not washed out, and the lower ones to the lithium carbonate obtained. In nine analyses carried out to test the phosphate method from 98.9 to 100.6 per cent with an average of 99.61 per cent was obtained.

In a still later article <sup>1</sup> Rammelsberg insisted that the phosphate precipitate always contains sodium, though Mayer <sup>2</sup> claimed this statement to be untrue. Some years later in a paper on the constitution of lithia micas, Rammelsberg <sup>3</sup> reviewed his results obtained since 1850, when he first used ether-alcohol in some tourmaline analyses and obtained values lower than those obtained by other analysts, who used the phosphate method of precipitation. He noted the loss of lithium in case the mixed chlorids were extracted only once and recommended that the residue be dissolved, dried, and extracted again. He tested his potassium platonic chlorid precipitates by igniting, weighing the  $2\text{KCl} + \text{Pt}$ , washing out the potassium-chlorid, and weighing the platinum and found the proportion of platinum less than that required for the theoretical composition of potassium platonic chlorid ( $\text{K}_2\text{PtCl}_6$ ) and therefore argued that no lithium was present, as lithium would have made the ratio of platinum larger. He did not note the testing of any of his residues or precipitates with the spectroscope. In another observation <sup>4</sup> on the lithium determination, he gave an analysis of a phosphate precipitate where the solution was strongly alkaline with sodium hydroxid before evaporation, and yet the precipitate gave phosphoric acid ( $\text{P}_2\text{O}_5$ ) 60.41 per cent, lithium oxid ( $\text{Li}_2\text{O}$ ) 37.14 per cent, sodium oxid ( $\text{Na}_2\text{O}$ ) 1.51 per cent; total, 99.06 per cent. When more sodium hydroxid was used the precipitate contained more sodium.

JENZSCH <sup>5</sup> in some analyses of minerals found a lithium platonic chlorid precipitated with his potassium platonic chlorid. He found it hard to extract all the lithium with ether-alcohol, and if he continued the treatment until all the lithium was in solution he had weighable quantities of sodium and potassium also dissolved. He made some experiments on the volatility of the lithium chlorid and sulphate and noted the much greater volatility of the chlorid and the tendency of the lithium chlorid to decompose and change into the hydroxid, which makes uncertain the weight of the mixed chlorids.

<sup>1</sup> Pogg. Ann., 1857, 102: 441-3.

<sup>2</sup> Ann. Chem. Pharm., 1856, 98: 193.

<sup>3</sup> Pogg. Ann., 1879, (2) 7: 136-146.

<sup>4</sup> Pogg. Ann., 1879, (2) 7: 157.

<sup>5</sup> Pogg. Ann., 1858, 104: 102.

BUNSEN<sup>1</sup> in the analysis of some alkali residues from lepidolite determined lithium as well as rubidium indirectly. He said that the determination by extraction of the mixed chlorids by ether-alcohol was as inaccurate as the determination as phosphate. His indirect method has not been used, however, by many other investigators. Like most indirect methods, there is a multiplication of error on the smaller constituent when one of the substances to be determined is present in much smaller quantity than the other. In addition, as Gooch<sup>2</sup> notes, there is the uncertainty in the total weight due to the behavior of the lithium chlorid when heated to dryness and the possibility of precipitation of lithium with the potassium as a double chlorid of lithium and potassium.<sup>3</sup>

FRESENIUS<sup>4</sup> repeated some of the work of Mayer<sup>5</sup> and found the objections of Rammelsberg<sup>6</sup> to be groundless. He evaporated to dryness with sodium phosphate and sodium hydroxid, the solution of the lithium chlorid with small quantities of sodium and potassium chlorids, separated from the greater part of the other alkaline chlorids by alcohol. The residue, taken up with a little water, was allowed to stand 12 hours after the addition of a little ammonia and the precipitate then separated by filtration and washed with equal parts of strong ammonia and water. He found on evaporating the filtrate and wash water and taking up the residue that a weighable precipitate of lithium phosphate remained even on the fourth evaporation. These analyses led him to agree with Mayer that it consisted of tri-basic lithium phosphate ( $\text{Li}_3\text{PO}_4$ ) without any sodium. The precipitate as formed contained water, but dried at  $100^\circ \text{C}$ . or gently ignited gave the lithium phosphate. He stated<sup>7</sup> that if the lithium phosphate left a residue insoluble in dilute hydrochloric acid, this should be separated, weighed, and its weight subtracted from that of the phosphate precipitate, and that if the solution moderately diluted gave a precipitate with ammonia, this should be separated and its weight taken from the original weight of lithium phosphate. This method, given in the text-book of Fresenius, was in use in the Fresenius laboratories at Wiesbaden in 1908.<sup>8</sup>

KRAUT, NAHNSEN, and CUNO<sup>9</sup> made analyses of phosphates of lithium and sodium obtained by precipitating after the manner of Berzelius<sup>10</sup> from solutions containing varying proportions of lithium

<sup>1</sup> Ann. Chem. Pharm., 1862, 122: 347; 354.

<sup>2</sup> Loc. cit.

<sup>3</sup> Jenzsch, loc. cit.

<sup>4</sup> Zts. anal. Chem., 1862, 1: 42.

<sup>5</sup> Loc. cit.

<sup>6</sup> Pogg. Ann., 1857, 102: 441-3.

<sup>7</sup> Zts. anal. Chem., 1876, 15: 227.

<sup>8</sup> Investigation of Gertrudis-Sprudels, by H. Fresenius. Jahrbücher des nassauischen Vereins für Naturkunde, 1908, p. 61.

<sup>9</sup> Ann. Chem. Pharm., 1876, 182: 165.

<sup>10</sup> Loc. cit.



chlorid and sodium pyrophosphate. By varying the proportion of sodium pyrophosphate to lithium chlorid from 20 to 1, to 2 to 1, the percentage of lithium oxid in the precipitate varied from 10 per cent to 24 per cent. One part of lithium chlorid to 10 parts of crystallized sodium pyrophosphate gave a precipitate of the composition found by Berzelius.

MERLING<sup>1</sup> made analyses of different phosphates of lithium and was able to obtain figures corresponding to the formulas  $\text{Li}_3\text{PO}_4$ ,  $\text{LiPO}_3$ , and  $\text{Li}_4\text{P}_2\text{O}_7$ . He found in using the phosphate method of separation as used by Fresenius<sup>2</sup> that the third evaporation of the filtrate gave him only 0.6 mg of insoluble phosphate. His total precipitate contained 6.8 mg of silica, which, subtracted from the amount of phosphate, left exactly the theoretical amount to be obtained from the lithium carbonate he started with, that is 104.53 per cent instead of 104.50 per cent.

GINTL<sup>3</sup> separated the lithium from the greater part of the other alkali salts by extraction with strong hydrochloric acid until the residue was free from lithium. He then evaporated the solution and repeated the extraction on the new residue until the amount of other alkali chlorids was small enough to permit the separation of the lithium either as phosphate or by ether-alcohol.

GOOCH,<sup>4</sup> reviewing the methods of Mayer and Rammelsberg and finding neither completely satisfactory, made the separation of the lithium chlorid from the chlorids of sodium and potassium by means of amyl alcohol. In his test experiments he separated from 0.01 to 0.1 gram of lithium chlorid from 0.1 or 0.2 gram of sodium or potassium chlorids. Haywood,<sup>5</sup> before publishing the Gooch method as a regular procedure for water analysis, verified the results obtained by Gooch and determined the value of the method in the separation of the small amounts of lithium usually found mixed with large amounts of other salts in mineral waters.

CARNOT<sup>6</sup> made a separation based on the differing solubilities of the alkaline fluorids. One part of lithium fluorid he found soluble in 800 parts of water, 1 part in 1,900 parts of a mixture of equal volumes of ammonia and water, and 1 part in 3,500 parts of a strongly ammoniacal solution of ammonium fluorid. It took, however, 70 parts of this reagent to dissolve 1 part of sodium fluorid. In the application of this method a solution of ammonium fluorid with an excess of ammonia was added to the concentrated solution of the mixed chlorids. After standing, the precipitate was washed

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<sup>1</sup> Zts. anal. Chem., 1879, 18: 563.

<sup>2</sup> Loc. cit.

<sup>3</sup> Ber. österreich. Ges. chem. Ind., 1880, p. 106.

<sup>4</sup> Amer. Chem. J., 1887, 9: 33-51.

<sup>5</sup> U. S. Dept. Agr., Bureau of Chemistry Bul. 91, p. 29.

<sup>6</sup> Bull. soc. chim. Par., 1889, (3) 1: 280.

by decantation and then on the filter with the precipitating reagent. The lithium fluorid was converted into sulphate and weighed. The filtrate, amounting usually to from 30 to 40 cc, was measured and 4 mg added to the weight of lithium sulphate for each 7 cc of the filtrate and wash water. Carnot gave some very good results obtained in the separation of lithium from a mixture of lithium carbonate, sodium carbonate, and potassium nitrate. For the determination of lithium in mineral waters<sup>1</sup> he removed the iron, silica, sulphate, magnesium, barium, calcium, and ammonium, leaving the alkaline chlorids with some magnesium, and verified the absence of lithium from each precipitate by the spectroscope. The mixed chlorids were extracted with alcohol to separate the lithium with some sodium and potassium from the main part of the sodium and potassium. When the residue was free from lithium the alcoholic solution was evaporated down, the residue taken up with water, and the lithium separated as fluorid. The magnesium with the lithium sulphate was precipitated as ammonium magnesium phosphate, ignited, weighed as pyrophosphate, calculated back to magnesium sulphate, and the weight subtracted to obtain the weight of lithium sulphate.

WALLER,<sup>2</sup> in the determination of the lithium in some well-known waters made use of Carnot's method as a check on the Gooch method. He found that from amounts of salts as large as one or two grams the amyl alcohol extraction was not satisfactory. In two lots he found on the first extraction 0.2400 gram and 0.2354 gram of lithium sulphate, and in the insoluble part 0.0974 gram and 0.0943 gram. The writers have often extracted the lithium chlorid from quantities of other alkalis amounting to over a gram and have found very slight spectroscopic traces in the insoluble part after two extractions. In the determination of lithium in one water the following results were obtained in two lots:

*Separation of lithium by two extractions of mixed chlorids.*

Sam- ple.	Weight of mixed chlorids.	1st extraction.		2d extraction.		Total lithium sulphate (Li <sub>2</sub> SO <sub>4</sub> ).	Lithium sulphate per gram of salts.
		Lithium sulphate (Li <sub>2</sub> SO <sub>4</sub> ).	Amyl alco- hol.	Lithium sulphate (Li <sub>2</sub> SO <sub>4</sub> ).	Amyl alco- hol.		
	<i>Grams.</i>	<i>Gram.</i>	<i>cc</i>	<i>Gram.</i>	<i>cc</i>	<i>Gram.</i>	<i>Gram.</i>
1	1.962	0.0187	24.5	0.0015	16.0	0.0202	0.0103
2	1.780	.0171	25.0	.0008	18.3	.0179	.0101

When the other chlorids separated from a solution containing nearly 0.001 gram of lithium chlorid per cc, it was not surprising that nearly 2 grams of salts should carry down 1 or 2 mg of lithium chlorid. When, however, as on the second extraction, the separation of the

<sup>1</sup> Bull. soc. chim. Par., 1889, (3) 1: 283-6.

<sup>2</sup> J. Amer. Chem. Soc., 1890, 12: 214.



other chlorids was from a solution containing only about 0.0001 gram of lithium chlorid per cc, it was not to be expected that much lithium would be found in the insoluble portion. It seems probable that Waller might have extracted all the lithium in his experiments by two more extractions. Although his figures for total lithium sulphate agree well, it is possible that the figures obtained by Carnot's method are high on account of the correction, which assumes that the filtrate and wash water were saturated with lithium fluorid, which may not always be the case.

In discussing the difficulties attending the complete separation of the lithium, sodium, and potassium from the other substances, Waller called attention to the necessity for careful cleaning of the platinum wires used in testing, as after holding a wire in the flame until the lithium line is no longer observed in the spectroscope, the line may reappear when the wire is moistened with hydrochloric acid and again brought into the flame. He noted that the barium carbonate and barium sulphate precipitates may carry down perceptible amounts of lithium. To lessen the error from this source he advises the precipitation of the sulphate in dilute solution followed by thorough washing to remove the lithium and recommended the solution and reprecipitation of the carbonate. He made no quantitative experiments on the subject, but considered that his experience confirmed Mayer's remark that under the influence of heat in the presence of water, the lithium chlorid had a tendency to exchange chlorin for oxygen. In his tests of the phosphate method he found lithium even in the first filtrate upon taking up the soluble material from the precipitate.

RANZOLI<sup>1</sup> in a comparison of different methods of separation of lithium obtained the following errors: By Mayer's<sup>2</sup> phosphate method when working with quantities of from 0.2452 to 0.5200 gram, the losses were from 0.0097 gram to 0.0176 gram, equivalent to an average of 3.05 per cent. By Carnot's<sup>3</sup> method he obtained 0.4780 gram and 0.4797 gram instead of 0.5200, showing losses of 0.0470 and 0.0403 gram, or equivalent to 7.9 per cent. By Gooch's<sup>4</sup> method he obtained 0.4907 and 0.4969 gram instead of 0.5200, losses of 0.0293 and 0.0231 gram, or equivalent to 5 per cent. He said that all the gravimetric determinations were carried out with all the precautions recommended by the authors. Of course in the analysis of mineral waters one rarely has to deal with quantities of lithium sulphate as great as 0.5 gram, and the quantity of mixed chlorids from a natural water which would contain such an amount of lithium would be entirely too large to handle as a matter of quantitative analysis. Nevertheless, from experience with the Gooch method it is the opin-

<sup>1</sup> Gaz. chim. ital., 1901, 31 (I): 40-48.

<sup>2</sup> Ann. Chem. Pharm., 1856, 98: 193.

<sup>3</sup> Bull. soc. chim., Par., 1880, (3) 1: 280.

<sup>4</sup> Amer. Chem. J., 1887, 9: 33-51.

ion of the authors that if the directions are closely followed no such error amounting to 0.029 gram is possible except from gross carelessness. Ranzoli remarked that all the gravimetric results are liable to be high on account of incomplete separation of the other alkalis from the lithium precipitate, or low because of the solubility of the lithium salt when the washing is complete enough to remove the others.

KAHLENBERG and KRAUSKOPF<sup>1</sup> devised a separation of lithium by pyridin. They found the chlorids of sodium and potassium to be practically insoluble in pyridin, while lithium chlorid is quite easily soluble. To make the separation, the mixed chlorids were evaporated to complete dryness with a little hydrochloric acid and the dry mass extracted once or twice with boiling pyridin which was filtered off. The pyridin was evaporated off from the insoluble residue which was dissolved in a little water, evaporated to dryness from hydrochloric acid and the extraction repeated. The pyridin solution was evaporated to dryness, treated with water and sulphuric acid and the lithium weighed as sulphate after evaporation and gentle ignition. The great advantage of the method is the freedom from corrections due to solubility of the other alkalis, which must be allowed for in the method of Gooch and probably should be allowed for in the use of the ether-alcohol extraction as usually carried out.

Kahlenberg and Krauskopf also mention the advantage of pyridin over amyl alcohol in the extraction of large quantities of lithium from moderate amounts of sodium salts. The smallest amount of lithium chlorid extracted by them was 0.090 gram from 0.83 gram of sodium chlorid and in another experiment 0.0907 gram from 0.1933 gram of potassium chlorid, 0.2913 gram of sodium chlorid, and 0.1021 gram of barium chlorid. Few natural waters have more than 1 per cent of lithium chlorid in the alkaline chlorids, so that to obtain for extraction a residue of mixed chlorids of which about 10 per cent would be lithium chlorid, it would be necessary to concentrate the lithium by alcohol or by hydrochloric acid extraction from the main bulk of the chlorids.

The pyridin extraction has been used by the authors on some mixed sulphates obtained by the Gooch method which were thought to contain too much sodium and potassium. The sulphate was removed by adding to the solution of the sulphates a slight excess of barium chlorid and filtering. The filtrate was evaporated to dryness and extracted with pyridin. As a check the material insoluble in pyridin was converted into sulphate and weighed, the sulphate taken up with water, filtered, and the filter paper with the barium sulphate burned in the dish and weighed with the dish to give the weight of the sodium and potassium sulphates.

<sup>1</sup> J. Amer. Chem. Soc., 1908, 30: 1104.

The following is a tabular statement of the results obtained:

*Separation of lithium from sodium and potassium by pyridin.*

Extraction.	First extraction with amyl alcohol.		Second extraction with amyl alcohol.		Total.	
	Li <sub>2</sub> SO <sub>4</sub> .	Na <sub>2</sub> SO <sub>4</sub> +K <sub>2</sub> SO <sub>4</sub> .	Li <sub>2</sub> SO <sub>4</sub> .	Na <sub>2</sub> SO <sub>4</sub> +K <sub>2</sub> SO <sub>4</sub> .	Li <sub>2</sub> SO <sub>4</sub> .	Na <sub>2</sub> SO <sub>4</sub> +K <sub>2</sub> SO <sub>4</sub> .
No. 1:						
Amounts determined by calculation from the weights of mixed sulphates and volumes of amyl alcohol.....	Gram. 0.0187	Gram. 0.0028	Gram. 0.0015	Gram. 0.0018	Gram. 0.0202	Gram. 0.0046
Weights actually obtained after separation by pyridin.....	.0185	.0029	.0015	.0021	.0200	.0050
No. 2:						
Amounts determined by calculation from the weights of mixed sulphates and volumes of amyl alcohol.....	.0171	.0028	.0008	.0021	.0179	.0049
Weights actually obtained after separation by pyridin.....	.0174	.0029	.0009	.0019	.0183	.0048

The weights of sodium and potassium sulphates were calculated for the amyl-alcohol extractions, using the corrections obtained as described later for the solubility of sodium and potassium chlorids in this solvent. The sodium and potassium sulphates in the pyridin extraction, however, were directly determined. Here the amount of lithium chlorid was greater than that of the sodium and potassium chlorids, though probably less than that of barium chlorid. The insolubility of barium chlorid in pyridin makes the Kahlenberg method especially useful for such checking of the mixed sulphates.

The unpleasant odor of pyridin and the difficulty of preparing and keeping it sufficiently free from water are objections to the use of the method which are not quite so strong in the case of the amyl alcohol. The chief objection to the use of the pyridin method in water analysis is the fact that usually very small quantities of lithium chlorid are to be separated from large quantities of sodium and potassium chlorids.

To extract the lithium from the dried crystalline mixed chlorids is much more difficult than is the extraction with amyl alcohol, the advantage of the latter method lying in the fact that the extraction is made from a solution of the chlorids; hence there is not the danger of loss from occlusion.

LECCO<sup>1</sup> suggested the recovery of the lithium from the filtrate obtained in the regular course of analysis after the precipitation of the calcium and magnesium. He added sodium hydroxid, evaporated to dryness, volatilized the ammonium salts and proceeded according to Mayer's method. He gave results showing the recovery of a trace, 0.0243 gram, and 0.0115 gram of lithium oxid from solu-

<sup>1</sup> Zts. anal. Chem., 1910, 49: 286-287.

tions to which were added none, 0.0236 and 0.0118 gram, respectively. The solutions contained also 0.005 gram of silica, 0.0006 gram of ferric oxid and alumina, 0.0232 gram of calcium oxid, and 0.0254 gram of magnesium oxid. In view of the general opinion of the uncertainty of the phosphate method and the possibility of loss of lithium with the various precipitates and in the removal of ammonium salts by heat, it seems unlikely that many will attempt to determine lithium in this final magnesium filtrate.

MURMAN<sup>1</sup> found the phosphate method unreliable by reason of impurities with the phosphate precipitate which made it too high, but which when removed left too little lithium phosphate. In an effort to obtain a suitable organic solvent for the separation of lithium chlorid, he tried water-free pyridin, anilin, methylanilin, o-toluidin, and phenol. Of these pyridin was the only one to dissolve the lithium chlorid well. Anilin dissolved it a little, and the others did not dissolve it at all. He gave as a method of separation the treatment recommended by Kahlenberg and Krauskopf.<sup>2</sup> He filtered off and weighed the material which was insoluble after the ignition of the sulphate and which he considered ferric oxid and magnesium oxid and subtracted the weight from that of the sulphates. The insoluble material obtained when the sulphates are dissolved has usually been considered as consisting in part of silica, and often sufficient magnesium has been found to precipitate as phosphate from the sulphate solution. Murman stated later<sup>3</sup> that he had not read of the work of Kahlenberg and Krauskopf until after the publication of his paper.

#### METHOD USED IN THE BUREAU OF CHEMISTRY.

When the lithium is to be determined in the same portion of water as the other alkalis and the sulphate, the silica is first removed by two evaporations with hydrochloric acid. The filtrate and washings from the silica determination are concentrated to from 150 to 200 cc and the sulphate determined as barium sulphate. In cases where much sulphate is present it is precipitated according to the method of Johnston and Adams.<sup>4</sup> The occlusion of alkali salts by barium sulphate has been noted by many writers and carefully studied by Allen and Johnston<sup>5</sup> and Johnston and Adams. Their results were obtained on solutions containing quantities of alkaline sulphates and chlorids much larger than are usually met with in water analysis, On account of the difficulty of obtaining the chlorids in condition to be weighed it has been found expedient to evaporate such a quantity of water that not more than 0.3 to 0.5 gram of mixed chlorids are

<sup>1</sup> Zts. anal. Chem., 1911, 50: 171-174.

<sup>2</sup> Loc. cit.

<sup>3</sup> Zts. anal. Chem., 1911, 50: 273.

40061°—Bull. 153—12—3

<sup>4</sup> J. Amer. Chem. Soc., 1911, 33: 829-845.

<sup>5</sup> J. Amer. Chem. Soc., 1910, 32: 588-617.

obtained. Of this amount the lithium is usually not a very considerable part and so any danger of loss of lithium with the barium sulphate precipitate may be safely neglected.

NOTE.—In some experiments on the recovery of small amounts of lithium from a mineral water the barium sulphate precipitate was extracted for 40 hours with 100 cc of water and 10 drops of hydrochloric acid (specific gravity 1.1). The liquid was filtered off, evaporated to dryness, and taken up in 10 cc of water. When examined with the spectroscope the lithium line was barely visible, indicating the presence of about 0.0002 mg of lithium per cc, or 0.0002 mg in all. These precipitates were from waters containing from 0.0004 to 0.0060 mg of lithium with no perceptible variation in the amount of lithium from the different samples.

In the case of a water sample on which it is not desired to determine the sulphate the barium chlorid may be added to the original water moderately acidified and the whole quantity evaporated to dryness, taken up with water and a little hydrochloric acid, and filtered.

The filtrate from the barium sulphate is evaporated to dryness and gently ignited to remove ammonium salts. The residue is then taken up in from 50 to 200 cc of water, according to the amount of alkali salts present, and milk of lime added in decided excess, the amount of excess being unimportant, as the solution can not be more than saturated with calcium hydroxid. The solution is boiled and placed on the steam bath for half an hour to allow the magnesium hydroxid to precipitate. This precipitate should not contain much lithium in ordinary cases. With waters very high in alkalis it is sometimes advisable to dissolve the magnesium hydroxid in hydrochloric acid and reprecipitate with milk of lime in order to be sure that all the sodium and potassium are in solution.

To the filtrate, having a volume of about 200 cc, ammonium hydroxid and carbonate are added to precipitate the calcium and barium. The flask is placed on the steam bath until the flocculent precipitate becomes crystalline; then the liquid is filtered off into a platinum dish and the precipitate washed only once or twice and dissolved into the flask with hydrochloric acid, using little more than enough to dissolve the whole precipitate. The barium and calcium are precipitated as before and the filtrate and washings added to the first filtrate for evaporation. By gentle ignition the ammonium salts are driven off the residue from evaporation of the filtrates. The alkalis are taken up in a little water and filtered through a small filter into a 50 cc beaker, a little ammonium carbonate, some ammonia, and one or two crystals of oxalic acid added, and the beaker placed on the steam bath for an hour or more. The last traces of calcium and barium left in solution on account of the large volumes used and the possible action of carbon dioxid on the precipitate are thus precipitated out and filtered off. If more than a



very slight precipitate is formed at this point, the filtrate from it is evaporated, the ammonium salts driven off, the residue taken up in water, filtered, and tested again with ammonium carbonate and oxalate. This is repeated as many times as necessary until no further precipitate is obtained. The filtrate is evaporated to dryness in a platinum dish suitable for weighing, taken up with a little hydrochloric acid and water, and again evaporated. The dish is gently heated to drive off ammonium salts, and the mixed chlorids are heated nearly to fusion. When cool, the dish and contents are weighed and heated to constant weight with ignition barely to redness, avoiding prolonged heating.

While sodium chlorid will stand a high temperature for a long time, the potassium chlorid is slightly volatile, and lithium chlorid is considerably more so and in addition is liable to decomposition. Pure lithium chlorid in quantity is difficult to weigh by ordinary methods. On account of the heat necessary to drive off the water, there is danger of a slight loss from volatilization or decomposition of some of the salt. As usually found in waters, however, the amount of lithium is so small in proportion to the sodium that the chance of loss is much lessened. After bringing to constant weight, the mixed chlorids are dissolved in a few cubic centimeters of water and filtered through a small filter into a 100-cc Erlenmeyer flask. The filter paper with the small amount of insoluble matter is burned in the dish and the weight of the dish and ash subtracted from the previous weight gives the weight of sodium, potassium, and lithium chlorids.

The solution of mixed chlorids in the flask is boiled down (after the addition of a piece of platinum foil to reduce bumping) until the salts are about to crystallize out. Amyl alcohol is then added up to a volume of about 40 cc, a cork with thermometer and delivery tube inserted, the delivery tube joined to a condenser and receiver, and the contents of the flask boiled until the thermometer registers the boiling point of the amyl alcohol,  $130^{\circ}$  to  $132^{\circ}$  C. The flask is cooled, one or two drops of dilute hydrochloric acid added, and the distillation continued until the temperature of the vapor again reaches its highest point. The flask is then slightly cooled and the contents filtered through a small Gooch crucible with asbestos mat into a 50-cc graduated cylinder. The volume (usually from 10 to 25 cc, according to the amount of lithium expected) is noted, and the flask and crucible are washed two or three times with a few cubic centimeters of anhydrous amyl alcohol from which the water has been boiled out just before separating the lithium. The amyl alcohol solution containing the lithium chlorid with some sodium and potassium chlorids is evaporated to dryness in a platinum dish. To convert the chlorids into sulphates, the residue is

moistened with a little sulphuric acid and water and evaporated again. The organic matter is destroyed by repeated very gentle ignitions, the residue being washed down with water and a drop or two of sulphuric acid after each ignition, and the water evaporated off. When the organic matter is removed, the dish and contents are gently ignited to constant weight, which is usually accomplished about as soon as the organic matter is removed, as the last trace of it is hardly weighable, although it may be visible.

The sulphates of sodium, potassium, and lithium are dissolved in a small quantity of water and filtered through a small filter and the dish and filter carefully washed. The paper with contents is burned in the dish and the weight of dish and ash subtracted from the previous weight to obtain the weight of sodium, potassium, and lithium sulphates formed from the chlorids dissolved by the amyl alcohol. To the filtrate are added a few crystals of ammonium phosphate, and when they are dissolved a few drops of ammonia are added, the solution stirred, and allowed to stand overnight. If a small precipitate forms, it is collected, ignited, and weighed as magnesium pyrophosphate. The equivalent weight of magnesium sulphate is calculated and subtracted from the weight of the combined sulphates obtained from the amyl alcohol extraction. The figures given by Gooch are used to calculate the correction for the solubility of sodium and potassium chlorids in amyl alcohol. Gooch found the solubility of sodium chlorid in the boiling amyl alcohol to be 0.0041 gram in 100 cc, and for potassium chlorid 0.0051 gram in 100 cc. When calculated to sulphates, these become 0.0050 gram of sodium sulphate and 0.0059 gram of potassium sulphate, or 0.0109 gram of both. In his experiments Gooch found that the anhydrous amyl alcohol used for washing the insoluble residue dissolved no appreciable amount of sodium or potassium chlorid, so that no correction was necessary for the volume of amyl alcohol used in the washing. For every 10 cc of alcohol in the filtrate (exclusive of the amount used for washing) from which the chlorids are precipitated there is subtracted from the weight of sulphates of lithium, sodium, and potassium 0.00109 gram. In many cases the corrections amount to the total weight obtained within the limit of the weighing error of the work. In such cases the amount of lithium may be determined by the use of the spectroscope.

It is evident that for the determination of very small amounts of lithium no method depending on the precipitation of a lithium compound is entirely satisfactory, because the solubility of the least soluble compound may be so great as to give no precipitate at all. It seems equally unreasonable to expect complete extraction of very small amounts of lithium from large amounts of other salts either by ether-alcohol or pyridin. However, in the extraction by amyl

alcohol the lithium is extracted from solution, and the other salts are precipitated out, leaving the lithium behind in solution. If the residue from evaporation of a water is treated as described, there is almost no chance for loss of the smallest amount of lithium, and with pure reagents none will be added to the solution.

### SPECTROSCOPIC DETERMINATION OF LITHIUM.

#### REVIEW OF METHODS DESCRIBED IN THE LITERATURE.

TALBOT<sup>1</sup> in 1826 suggested that if it should be shown that the various colored lines of the spectrum were due to the different metals and were characteristic of them, "a glance at the prismatic spectrum of a flame may show it to contain substances which it would otherwise require a laborious chemical analysis to detect." Later<sup>2</sup> (1834) he decided that the minutest portions of lithium and strontium could be distinguished by optical analysis with as much certainty, if not more, than by any other method. In 1836<sup>3</sup> he said: "It is much to be desired that an extensive course of experiments should be made on the spectra of chemical flames with accurate measurements of the relative positions of bright and dark lines or maxima and minima of light which are generally seen in them." He used chiefly the spirit lamp for the production of spectral lines and mentioned<sup>4</sup> the use of a stream of oxygen with the flame of the spirit lamp, by which means he obtained much brighter flames with the salts of sodium, strontium, or barium.

KIRCHHOFF and BUNSEN<sup>5</sup> published their work on analysis by spectrum observations in 1860. Earlier observers had used ordinary luminous gas flames or alcohol flames for the production of the spectra while they used the burner described by Bunsen<sup>6</sup> a few years previously. Although Swan<sup>7</sup> had described the use of the collimator in 1856 and had suggested that the D line was due to sodium, the thorough study and mapping of the spectra by Kirchhoff and Bunsen is generally regarded as the beginning of the systematic use of the spectroscope for analysis. They studied the spectra of many salts of the alkalis and alkaline earths, using the flames of sulphur, carbon bisulphid, alcohol, gas with the Bunsen burner, carbon monoxid, hydrogen and oxy-hydrogen, and found that the lines had the same position with all flames, but were brighter as the temperature of the flames was higher.

They made some tests also of spark spectra of the metals and obtained the same lines. In order to obtain some idea of the sensi-

<sup>1</sup> Edin. J. Sci., 1826, 5: 77.

<sup>2</sup> Phil. Mag., 1834, (3) 4: 114.

<sup>3</sup> Phil. Mag., 1836, (3) 9: 3.

<sup>4</sup> Phil. Mag., 1833, (3) 3: 35.

<sup>5</sup> Pogg. Ann., 1860, 110: 161-180.

<sup>6</sup> Pogg. Ann., 1856, 100: 85.

<sup>7</sup> Phil. Mag., 1860, (4) 20: 173.



tiveness of the tests they burned chlorates with milk sugar to diffuse the vapors through the air and where the chlorate of a metal was not easily obtained they used some other salt with the chlorate of another metal not so easily detected by the spectroscope. Three milligrams of sodium chlorate burned with milk sugar in a room of about 60 cubic meters capacity caused a Bunsen burner in the room to show the sodium line in the spectroscope for 10 minutes. Considering that 1 second was enough time to make certain of seeing the line, they figured out that it required  $1/3,000,000$  mg of the sodium chlorate, which would be 0.00000006 mg of sodium. In a similar manner they determined that the least amount which they could see of lithium was 0.000002 mg, potassium 0.0003 mg, strontium 0.00003 mg, calcium 0.00002 mg, and barium 0.0006 mg. In some cases the products of the combustion of the salts and milk sugar were distributed throughout the air of the room by swinging an open umbrella.

Kirchhoff and Bunsen reported the presence of lithium in a large number of substances, in the ash of various plants, in minerals, and in many waters. They also made spectroscopic analyses of several water residues, obtaining the spectra of sodium, potassium, lithium, and calcium in sea water and strontium in the scale from boilers of ocean steamships. They also reported the experiments from which they concluded that the dark lines in the solar spectrum were caused by the absorption of light by the incandescent vapors of the substances which of themselves would give bright lines where the dark lines occurred. For introducing liquids into the flame they used a fine platinum wire with a loop at the end, the wire being slightly flattened at the loop. Substances which were not easily volatile they decomposed with hydrochloric acid or else ammonium fluorid and sulphuric acid. In the following year<sup>1</sup> they reported the discovery of rubidium and cæsium in the Durkheim mineral water. They could detect by the spectroscope 0.0002 mg of rubidium chlorid and 0.00005 mg of cæsium chlorid when using a drop of solution weighing 4 mg.

BREWSTER<sup>2</sup> in some notes on the history of spectrum analysis referred to his former publications<sup>3</sup> on the colored flames and spectra of substances and noted that in 1842,<sup>4</sup> after trying 124 substances in the flame of gas from oil and oxygen, he described the spectra of many substances.

SIMMLER,<sup>5</sup> in some qualitative studies of spectra of minerals and water residues, described the spectrum of the inner cone of the

<sup>1</sup> Pogg. Ann., 1861, 113: 337-381.

<sup>2</sup> Compt. Rend., 1866, 62: 17-18.

<sup>3</sup> Pogg. Ann., 1836, 38: 61-63; Phil. Mag., 1836, 8: 384; Trans. Edin. Phil. Soc., 1833, 12: 519; 544; 545.

<sup>4</sup> Rept. Brit. Assoc., 1842, p. 15.

<sup>5</sup> Pogg. Ann., 1862, 115: 242-266; 425.

Bunsen burner flame, which may interfere with the observation of the spectra desired, but which does not necessarily appear.

MITSCHERLICH<sup>1</sup> in spectrum observations fed the solution to the flame by means of a wick of platinum wires fastened into the bottom of a tube containing the solution. In later work<sup>2</sup> he used several other devices, such as mixing vapor of the substances with a combustible gas and burning the gas with oxygen. He volatilized the solid substance or solution by heat or an electric spark, while a stream of hydrogen passing through the vessel took up the vapor and, when burned with oxygen, gave the spectrum.

BRASSACK<sup>3</sup> made some experiments on the sensitiveness of the spectroscopic test with the spark. He measured the loss in weight of the points in one hour and calculated the loss per second which he considered the minimum amount of the metal which would give a spectrum.

CAPPEL<sup>4</sup> made a study of the sensitiveness of the spectroscopic tests for various elements. He used a spark from an induction coil and placed on one of the points a drop of solution weighing 1 mg. By this means he could detect 0.000000025 mg of lithium or one-seventieth the amount which Kirschhoff and Bunsen could detect by the gas flame. He found it necessary to use quantities of rubidium, caesium, and potassium six or seven times as great as the least quantities shown in the Bunsen flame.

CHURCH<sup>5</sup> used the spectroscope to test for lithium in studying the connection between different bodies of ground water. Where a quantity of lithium salt was put in one well, lithium could be detected in the water from a near-by well in a few hours. It is probable that this method would still be better than the application of common salt followed by a study of the chlorine content of the water in the second well, though it is not so satisfactory as the use of a suitable dye.

JANSSEN,<sup>6</sup> in the transactions of the British Association for 1869, referred to some experiments which he made with the sodium spectrum, using a luminous flame between the Bunsen burner and the slit of his spectroscope. When the sodium salt was brought into the flame the bright line of sodium could be seen in the continuous spectrum from the luminous flame. He expanded this note somewhat and published it<sup>7</sup> because he had suggested to Champion that a quantitative method might be developed from this idea, or else

<sup>1</sup> Pogg. Ann., 1862, 116: 499-507.

<sup>2</sup> Pogg. Ann., 1864, 121: 459-488.

<sup>3</sup> Zts. anal. Chem., 1865, 4: 87 (*abst.*).

<sup>4</sup> Pogg. Ann., 1870, 139: 628-639.

<sup>5</sup> Chem. News, 1870, 22: 322.

<sup>6</sup> Trans. Brit. Association for Advancement of Science, 1869, p. 68.

<sup>7</sup> Compt. rend., 1870, 71: 626, 629.

be based on the relation between the amount of sodium on a wire and the length of time required to volatilize it.

CHAMPION, PELLET, and GRENIER,<sup>1</sup> starting from the suggestion of Janssen, developed a method for sodium where the sodium line was extinguished by a blue glass made in the form of a wedge, with a corresponding wedge of plain glass after the fashion of the compensator in a saccharimeter. They calibrated the blue-glass wedge, obtaining the quantities of sodium, the bright line from which would just be extinguished by the prism in different positions. Working on soils, they were able to get fairly accurate figures for the sodium content. They determined the sodium always in a solution saturated with potassium sulphate. The mean of three determinations gave 0.297 gram of sodium oxid in 100 grams of water which contained 0.3 gram, and they found 0.63 gram in 100 grams of water containing 0.6 gram.

In a note<sup>2</sup> on the work of Champion, Pellet, and Grenier, Janssen referred to the value of approximate determinations at times and suggested again the value of a method based on the duration of the spectral lines.

LOCKYER and ROBERTS<sup>3</sup> made an attempt at the quantitative analysis of alloys by study of the spectra obtained by causing a spark to pass between points of the alloys. As one of the constituents of the alloys decreased in amount its lines disappeared from the spectrum. They obtained some figures as to the smallest amount of a metal which might be present in an alloy and show its lines in the spark spectrum.

TRUCHOT<sup>4</sup> made some determinations of lithium in waters by comparing the intensity and duration of the lithium line obtained from the sample with that obtained from standards. He made standards containing from 5 to 40 mg of lithium chlorid per liter. This method has been used in the investigations at the Bureau of Chemistry with the modification that standards were made containing in addition to the lithium different amounts of sodium chlorid, either 10 or 100 mg per cubic centimeter, and the mixed chlorids which were to be tested were dissolved in such an amount of water that the solution contained either 10 or 100 mg per cubic centimeter. Using a straight wire, 0.01 mg of lithium per cubic centimeter was about the lowest limit with a solution of lithium chlorid alone. When the solution of this strength contained 100 mg of sodium chlorid, the lithium line was very much more difficult to see. A straight wire with a rough surface will take up nearly the same amount of liquid each time, but unless considerable care is exercised the amount is too variable to give good quantitative results. The use of a small coil

<sup>1</sup> Compt. rend., 1873, 76: 707-11.

<sup>2</sup> Compt. rend., 1873, 76: 711-13.

<sup>3</sup> Proc. Roy. Soc. Lond., 1873, 21: 507-8.

<sup>4</sup> Compt. Rend., 1874, 78: 1022-1024.

of wire suggested by Truchot by which a fairly uniform drop of liquid is picked up each time is an improvement.

In Table I<sup>1</sup> are given some results showing the relative accuracy of readings made under strictly uniform conditions, using a straight wire and Bunsen lamp. Results are given on standards of known amounts of lithium chlorid without the addition of sodium chlorid, with varying amounts of lithium chlorid plus 10 mg of sodium chlorid per cubic centimeter, and with varying amounts of lithium chlorid plus 100 mg of sodium chlorid per cubic centimeter. The masking due to potassium was tested and found to be very much less than that due to sodium; therefore, in view of the small amounts of potassium usually found in mineral waters as compared with sodium, the effect of potassium was not studied further.

In order to avoid the personal equation as much as possible, the solutions were prepared by an assistant and read by two persons unacquainted with the value of the solutions, one analyst making two sets of observations but on different days. A preliminary test of the unknown solution at once showed whether the standards to be used for comparison should be the set containing 10 mg of sodium chlorid per cubic centimeter or that containing 100 mg of sodium chlorid per cubic centimeter. The appropriate set of standards for comparison was then selected. These standards were prepared in sets containing amounts of lithium varying from 0.01 to 1.00 mg per cubic centimeter, and the comparisons made in a manner suggested by the comparison of colorimetric standards.

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<sup>1</sup> Skinner, "A spectroscopic method for the determination of lithium," a paper read at the meeting of American Association for the Advancement of Science, 1908.

TABLE I.—*Determination of lithium by modified method of Truchot.*

## WITH NO SODIUM CHLORID.

Lithium added to solution (mg per cc).	Lithium found by comparison with standards containing the same amount of sodium chlorid.			Lithium added to solution (mg per cc).	Lithium found by comparison with standards containing the same amount of sodium chlorid.		
	Analyst A.		Analyst B.		Analyst A.		Analyst B.
	First day.	Second day.			First day.	Second day.	
0.70	0.50	0.50	0.50	1.00	0.80	0.90	0.80
.20	.10	.10	.30	.05	.08	.05	.04
.80	.70	.80	1.00	.80	1.00	.80	1.00
.01	.02	.01	.01	.40	.60	.50	.20
.05	.03	.03	.05	.01	.01	.01	.01

## WITH 10 MG SODIUM CHLORID PER CUBIC CENTIMETER.

0.01	0.03	0.02	0.01	0.05	0.06	0.10	0.10
.01	.02	.02	.01	.70	.80	.50	.50
.50	.50	.50	.30	.40	.80	.50	.40
.20	.20	.40	.30	.10	.10	.20	.08
1.00	.90	1.00	1.00	.30	.20	.25	.25

## WITH 100 MG SODIUM CHLORID PER CUBIC CENTIMETER.

1.00	0.80	.....	1.00	0.10	0.06	.....	0.20
1.00	.90	.....	1.00	.01	.04	.....	.00
.80	.60	.....	1.00	.02	.06	.....	.05
.20	.10	.....	.05	.03	.03	.....	.02
.50	.50	.....	.25	.04	.02	.....	.01

BALLMANN<sup>1</sup> diluted a solution containing a known amount of lithium until the lithium line could not be seen in the spectroscope, and then diluted the unknown solution to the point where the line could not be seen. By considering the concentration of lithium the same in both cases he was able to calculate the amount in the unknown solution. In his experiments the lithium line was seen easily with a volume of 1,320 cc, seen faintly twice and missed once when the volume was 1,340 cc, and with a volume of 1,360 cc could not be seen at all. This would appear to make the error of the method about 2 per cent. The lithium line could not be seen when 1 mg of lithium chlorid was made up to 3,345 cc (0.0003 mg in 1 cc). Ballmann used a spiral loop 2.5 mm in diameter and 3.5 mm along the axis.

JONES,<sup>2</sup> in a note concerning the work of Ballmann, described some of his own experiments on quantitative spectroscopic determinations. He diluted solutions until a measured volume, usually 0.3 cc, introduced into the flame failed to give the lines in the spectroscope. He used pellets of cotton or filter paper folded as for burning. The solution was absorbed by the porous material and after drying and burning off the combustible matter the ash which was left in a porous

<sup>1</sup> Zts. anal. Chem., 1875, 14: 297.<sup>2</sup> Chem. News, 1876, 34: 122.



state was strongly ignited to give the spectrum. He found that as the solution was diluted the spectra lost their brilliancy so slowly that it was very difficult to fix the point at which they disappeared. He considered it possible to estimate roughly the amount of potassium in a solution by this method, the error allowed being 10 times the quantity of metal to be determined. By trying, like Truchot, to match the intensity of lines he had no better success. He mentioned as the limit for potassium 0.0006 mg of potassium in the form of a salt. It seems possible that the error of 10 times the quantity sought should have read "0.1 times the quantity sought." Owing to the strain upon the eyes and the inaccuracy of the results, he gave up the attempt to use a spectroscopic method.

LIVEING and DEWAR<sup>1</sup> made some experiments on quantitative analysis by obtaining absorption bands due to small quantities of sodium vapor in iron tubes which were kept very hot. The results were not of any practical value.

BELL<sup>2</sup> published a description of a spectroscopic method for the quantitative determination of lithium which was identical with the method of Ballmann, as noted by Hofmann.<sup>3</sup> He used a small loop for bringing the solution into the flame and called attention to the necessity of keeping the flame of constant intensity and always bringing the loop into the same part of the flame. He developed the use of the method for lithium determinations, but stated that it might be used for other substances, especially thallium. Calcium, strontium, barium, and potassium, he said, do not give lines sufficiently persistent, except in strong solutions, which is true also of cesium and rubidium, while sodium is so ubiquitous as to give very uncertain results.

FOEHR,<sup>4</sup> commenting on Bell's<sup>5</sup> paper, stated that he himself had made many experiments on quantitative analysis by the spectroscope, but did not obtain as good results as those reported by Bell. Instead of diluting until the spectrum failed to appear, he added a solution of the substance a little at a time to pure water, testing the mixture by means of the spectroscope after each addition. The end point was the concentration at which the spectrum first appeared and was found to be much sharper by this method. He determined potassium by adding the solution of the potassium salt to a saturated solution of ammonium chlorid until the spectrum of potassium appeared, and also made determinations by adding an excess of ammonium chlorid solution to the unknown potassium solution, then adding solution of known potassium content until the potassium line appeared again. Foehr stated that the lithium line is much more

<sup>1</sup> Proc. Roy. Soc., Lond., 1879, 29: 482-489.

<sup>2</sup> Amer. Chem. J., 1885, 7: 35.

<sup>3</sup> Ber. d. chem. Ges., 1885, 18: 2897.

<sup>4</sup> Chem. Ztg., 1885, 9: 1613.

<sup>5</sup> Amer. Chem. J., 1885, 7: 35.

easily seen from lithium chlorid solution than from a solution of lithium sulphate of equivalent concentration, with which statement the authors can not entirely agree, for in their work they have found the amount of lithium required to show the lithium line in the spectroscopie to be about the same whether it is present in solution as the sulphate or chlorid.

GOOCH and HART<sup>1</sup> determined potassium by the use of the spectroscopie by matching the intensity of the red line of potassium in known and unknown solutions. They used a Bunsen burner and brought the solution into the flame on a spiral coil holding 0.020 gram of solution and found that the brilliancy of the red line in the potassium spectrum was increased by the presence of sodium salts until the amount of sodium was 100 times that of the potassium, after which more sodium made the potassium line appear less distinct. Therefore they made their potassium standards to have about the same concentration of sodium as the unknown solution and reported very close results in their test analyses.

GOOCH and PHINNEY<sup>2</sup> determined rubidium by a method similar to that of Gooch and Hart for potassium. The interference of potassium with the rubidium determination was more marked than the interference of sodium with potassium. Working with 1, 2, and 1 mg of rubidium in rubidium chlorid with 0.1 gram of potassium as chlorid, they precipitated the greater part of the potassium salt by alcohol and then found 0.8, 1.7, and 0.9 mg of rubidium, respectively, showing errors of from 10 to 20 per cent.

NASINI and ANDERLINI<sup>3</sup> determined lithium in a thermal water by the method of Foehr. At another time<sup>4</sup> in the analysis of a brine they used this method on the original water, first obtaining a rough approximation as to the amount and then making up a solution with a known amount of lithium and about the same content of other substances as the water under examination. When this solution was added to distilled water and tested with the spectroscopie the amount of lithium present when the lithium line first appeared was different from the amount required when no other salts were present. They noted the necessity of having the wires and drops of uniform size, of keeping the Bunsen burner flame of constant size, and of always placing the wire in the same part of the flame.

VOGEL<sup>5</sup> studied the different methods of producing flame spectra and concluded that for general use the illuminating gas-oxygen flame was the most satisfactory as the spectra were brighter than with the Bunsen burner flame. He made lists of the elements best studied by the Bunsen burner flame, the illuminating gas-oxygen

<sup>1</sup> Amer. J. Sci., 1890, (3) 42 : 448.

<sup>2</sup> Amer. J. Sci., 1892 (3) 44 : 392-400.

<sup>3</sup> Gaz. chim. ital., 1894, 24 (I) : 327.

<sup>4</sup> Gaz. chim. ital., 1890, 20 (I) : 305.

<sup>5</sup> Zts. anorg. Chem., 1894, 5 : 42-62.

flame, the spark, and by absorption, reporting lithium as best shown in the gas-oxygen flame.

RANZOLI,<sup>1</sup> comparing the spectroscopic and gravimetric methods for lithium after obtaining the results quoted above (p. 14), determined the lithium by Foehr's method and found 0.52078, 0.51688, and 0.5151 gram of lithium chlorid instead of 0.54 gram, the average being 4.15 per cent low. Then he used the method as modified by Nasini and Anderlini<sup>2</sup> and found 0.53612 and 0.53914 instead of 0.5400 gram. On some solutions of unknown lithium content he obtained 0.2708 gram when the solution contained 0.2700 and obtained 0.18953 gram from a solution containing 0.189 gram. The average error on the three solutions was 0.365 per cent. Ranzoli advocated the use of this method in preference to the gravimetric method for all waters, as the determination is made on the original water added to distilled water and there is no chance for loss or gain of lithium in manipulation.

HERMANN,<sup>3</sup> in some investigations on the presence of lithium in the human body, determined the presence of lithium by the spectroscope. With the apparatus used, he could detect 0.0002 mg per cubic centimeter. He used a drop of 0.01 cc volume.

NUTTING,<sup>4</sup> working with the spectra of alloys, confirmed to a certain extent Lockyer's<sup>5</sup> supposition that arc spectra might be used for quantitative analysis of alloys. He said (par. 4, p. 137):

4. Spectroscopic quantitative analysis to within an error of perhaps 5 per cent appears to be practicable, provided: (a) Selected lines of similar character are used for comparison; (b) spectra are taken with an arc or spark with capacity and inductance, with sufficient current to produce plenty of metallic vapor in proportion to the ambient gas; (c) allowance is made for difference in the natural intensity and hardness of the spectra of various pure metals taken under the same conditions; (d) allowance is made for differences in the atomic weights of components, provided these differ by a considerable amount.

ABATI<sup>6</sup> determined the lithium in a mineral water by the method of Nasini and Anderlini. He used a bunsen burner with the center of the flame 4 cm from the slit of the spectroscope, which had a width of 0.2 mm. He used a loop made from wire 0.17 mm in diameter wound in six turns, making a spiral 1.82 mm in diameter and 1.1 mm high. The loop was filled with solution, the water gently evaporated and the dry loop brought into the flame. The water to be examined was diluted until the lithium line was barely visible. This diluted solution was added, a little at a time to 25 cc of water until the line appeared in the spectroscope. At first the standard

<sup>1</sup> *Gaz. chim. ital.*, 1901, 31 (I) : 40-48.

<sup>2</sup> *Gaz. chim. ital.*, 1890, 30 (I) : 305.

<sup>3</sup> *Über das Vorkommen des Lithions im menschlichen Organismus*, 1905.

<sup>4</sup> *Astrophys J.*, 1905, 22: 131-137.

<sup>5</sup> *Lec. cit.*

<sup>6</sup> *Gaz. chim. ital.*, 1906, 36 (II) : 855-860.



solution was made up according to a former analysis of the water which gave 0.047 gram per liter of lithium. A rough comparison showed that this solution contained about twelve times as much lithium as the sample for analysis; therefore, a new solution was prepared with the same amounts of sodium, potassium, and calcium chlorids, and one-twelfth as much lithium. When 147 cc of this solution were added to 25 cc of distilled water the line lithium could not be seen. With 148 cc one trial gave the lithium line, while with 149 cc the majority of the drops taken showed the line, and when 150 cc were added every drop tried gave the line. One hundred and forty-seven cubic centimeters of the water mixed with 25 cc of distilled water failed to show the lithium line, with 148 cc added the line appeared in a majority of the trials, and with 149 cc added it was shown by every drop. These readings would indicate an error of less than 1 per cent in the determination which is a greater accuracy than we have regularly obtained when working with this method.

MOTTRAM<sup>1</sup> determined the amounts of sodium and potassium in tissues by a spectroscopic method depending on the relation between the weight of the substance and the time it required to completely volatilize in the flame as shown in the spectroscope. He found that it took 6.5 minutes to volatilize 0.001 mg of sodium as sulphate and that the presence of other substances and the acid radical combined with the metal affected the time required for volatilization. This is an extension of the method of Truchot,<sup>2</sup> and the suggestion of Janssen<sup>3</sup> in regard to the use of the duration of the spectrum as a measure of the amount of material. Using a straight wire we made some rough tests of this suggestion when using Truchot's method. The results were not entirely satisfactory.

HEMPEL and KLEMPERER<sup>4</sup> devised a complicated method for obtaining quantitative results by spectroscopic analysis of soils. It is much like one of the methods used by Mitscherlich.<sup>5</sup> They used a spark to volatilize water over which was passed hydrogen which was burned with oxygen before the slit of the spectroscope. A solution of known content of lithium or potassium was let into the vessel until the lithium or potassium line was shown in the spectroscope, and a solution of the soil then added to the water with the passage of the spark, and when the oxyhydrogen flame gave the spectrum of lithium or potassium the quantity present could be calculated. From 0.0082 to 0.035 per cent of lithium oxid was found in various ignited soils, with an average value of 0.0148 per cent for 10 soils.

While Nasini and Anderlini, Ranzoli and Abati all gave most excellent results obtained by the method used by Nasini and Ander-

<sup>1</sup> Arch. Middlesex Hosp., 1909, 15: 106-117.

<sup>2</sup> Compt. rend., 1874, 78: 1022.

<sup>3</sup> Compt. rend., 1873, 76: 711-713.

<sup>4</sup> Zts. angew Chem., 1910, 23: 1756-1759.

<sup>5</sup> Pogg. Ann., 1864, 121: 459-488.

lini, such close results have not been obtained when using this method in the Bureau of Chemistry. When, therefore, lithium is present in weighable amounts, and reasonable quantities of water are available for examination, the amyl alcohol separation is preferred. On the other hand, the results obtained in the Bureau of Chemistry do not agree with the statement of Kayser<sup>1</sup> that no satisfactory quantitative analyses can be made by the spectroscope. For the estimation of lithium in many waters on which work has been done, the method of Nasini and Anderlini could not be used because the waters contained so little lithium that the spectrum could not be obtained from the water without considerable concentration. As in most of the work complete analyses were required, the alkaline chlorids were obtained pure, so that it was very little trouble to separate the lithium by amyl alcohol, and when it was separated the lithium could be determined by the spectroscope. The extraction with amyl alcohol from the solution of the chlorids seemed the only way likely to give all the lithium when the total amount was less than 1 mg. On account of the fact that the lithium always remained in solution, there was no serious trouble from either of the difficulties mentioned by Ranzoli as objections to the gravimetric methods.

#### METHOD USED IN THE BUREAU OF CHEMISTRY, WITH EXPERIMENTAL DATA.

After the preparation of the sulphates of sodium, lithium, and potassium for weighing, they are dissolved in a small amount of water, from 1 to 10 cc according to the amounts of lithium expected to be found. By trying the solutions in the flame before the spectroscope it was quickly determined whether to dilute to the vanishing point of the lithium line, as did Ballmann<sup>2</sup> and Bell,<sup>3</sup> or whether to make to a volume of 25 to 100 cc and add to distilled water as Foehr did. In consideration of the errors of observation, it has not seemed worth while to add sodium and potassium sulphates to the lithium solution used for comparison. The potassium and sodium sulphates are rarely present to the amount of more than 0.0005 gram each or at the most 0.0010 gram each. In most cases the potassium spectrum does not appear at all in the work and the sodium line is not much brighter than it is in the lithium solution of known strength which has been kept in a glass bottle for a short time. The spectroscope used in the investigations is an ordinary high-grade instrument made by Krüss. The scale is illuminated by a small electric light, and switches under the edge of the table enable the observer to illuminate the scale or the room without moving.

<sup>1</sup> Handbuch der Spectroscopie, 1910, 5: 24.

<sup>3</sup> Amer. Chem. J., 1885, 7: 35.

<sup>2</sup> Zts. anal. Chem., 1875, 14: 297.

Most of the experimental work has been done with a Bunsen burner having a rather small tip, which makes the flame steadier. A porcelain burner was used to eliminate the copper lines which occasionally appeared, but as in most of the work the telescopes were set so as to have the sodium line just barely out of the field, no other spectra came into view to interfere with the observation of the lithium line. A hydrogen flame which, from some preliminary trials, gave promise of overcoming several difficulties encountered with other sources of heat was also used. With the burner which was devised for use with hydrogen and the apparatus for supplying the gas the variations in the intensity of the flame over a period of several hours could not be controlled as well as could be done with a Bunsen burner and ordinary gas, and it was finally concluded that the advantages of the hydrogen flame were not sufficient to warrant an elaborate apparatus for controlling and supplying the gas at fairly constant pressure over extended periods of time.

To bring the solution into the flame, platinum wires are used which are formed into cylinders at the ends by winding four times about a No. 10 wire. The four turns lie close together making almost a solid cylinder, and drops picked up in these loops are very constant in weight, some of the first loops used containing 0.010 to 0.012 gram of water. The cold loop is carefully plunged into the solution and taken out with the axis of the cylinder parallel to the surface of the water. The drop of water is carefully evaporated by placing it at such a distance above a flame that it is vaporized without spattering. The loop is then brought into the flame, usually after being warmed a little. With the apparatus as used regularly in the Bureau of Chemistry different observers usually have about the same limit for the amount of lithium which will barely show the lithium line. This varies from 0.000015 to 0.000025 mg per cc when no large amounts of other alkalis are present.

There is a possible chance for some slight variation in the amount of solution taken up by the loop, but weighings of the amounts taken up in many successive trials indicated that this is a wholly negligible source of error. The bringing of the loop into the flame is probably the chief source of error. None of the authors using a platinum wire made any mention of the difficulty of accomplishing this in a uniform manner. If the loop is made of moderately fine platinum wire, the wire is not likely to be perfectly straight, so that if it is held in a stand great care is needed to have the loop always at the same height. It would be entirely feasible to arrange a mechanical holder which would insure the proper placing of the loop in the flame, but it has been found more convenient to have one person put the loop into the flame while another makes the observation. With care and experience the one handling the wire can place it in the flame with the loop always

at the same height, using some object or part of the spectroscope as a gauge. When nearly at the limit of visibility of the lithium line he can make the line appear or not by varying the vertical position of the loop in the flame less than a centimeter. The position of the loop in the horizontal section of the flame also affects the brilliance of the lithium line, probably due in part to the distance from the slit. It requires some practice and skill, therefore, on the part of the assistant holding the wire if concordant results are to be obtained.

In fact, the success of the observations depends upon maintaining strictly comparable conditions throughout an observation on both standard and unknown solutions. One of the chief reasons for trying the hydrogen flame was to lessen the variations due to the uncertainty of the position of the loop before the slit. With the conveniences at hand for controlling the supply of hydrogen, however, there were greater irregularities introduced by the varying size of the flame than were due to the position of the loop in the flame. With the use of illuminating gas it has been found that the pressure varies during the day so as to cause some slight irregularity in the minimum amount of lithium necessary to produce a spectrum and it is desirable to check the standard frequently. The distance from the slit in the collimator to the flame is a factor which may be kept constant, as may the width of the slit. The following figures show something of the effect of the width of the slit on the sensitiveness of the test. These trials were made with the hydrogen flame.

*Effect of the width of slit of collimator on the sensitiveness of the test.*

Width of slit of collimator.	Observed limit of lithium (per cubic centimeter).	Width of slit of collimator.	Observed limit of lithium (per cubic centimeter).	Width of slit of collimator.	Observed limit of lithium (per cubic centimeter).	Width of slit of collimator.	Observed limit of lithium (per cubic centimeter).
<i>mm</i>	<i>mg</i>	<i>mm</i>	<i>mg</i>	<i>mm</i>	<i>mg</i>	<i>mm</i>	<i>mg</i>
0.04	0.000058	0.05	0.00006	0.14	0.000014	0.24	0.000012
.06	.000022	.06	.00004	.16	.000013	.30	.000010
.08	.000017	.08	.000019	.18	.000013	.20	.000010
.12	.000010	.10	.000015	.18	.000010	.16	.000012
.04	.00007	.12	.000014	.20	.000011	.12	.000015

Up to about the width of 0.2 mm the lithium line is visible with smaller amounts of lithium as the slit is made wider. If used wider than 0.2 mm there is no very noticeable increase in brilliance in the lithium line while if other salts are present the light from them is so bright as to interfere seriously with the observation of the lithium. As the whole method rests upon the fact of the observer seeing or not seeing the lithium line, there enters also a question of the personal equation. In all experiments it is possible to keep the mind of the observer free from bias. No effect of the observer's

desire or expectation has been noted on the visibility of the lithium line and so no special effort has been made to keep him in ignorance. There has been an attempt to make the dilutions such that the relations could not be readily calculated, so that each determination of limiting concentration was independent of the others on the same solution.

While working at determinations with the spectroscope the element of fatigue enters as Jones<sup>1</sup> observed and the eye may become less sensitive. On the other hand, up to a certain time it is quite likely that the eye becomes more sensitive with practice. If a complete determination could be carried out with trials at only six or seven dilutions as given by Abati,<sup>2</sup> it is not likely at any time that the condition of the observer would enter very largely into the results, but it usually requires a number of trials to come anywhere near the proper dilutions where the final trials may be made. The suggestions given in the following description of the method should therefore be carefully observed.

To show what results could be obtained by the method outlined, four samples were taken through the regular procedure for the determination of lithium when present in small quantities; that is, the silica, sulphates, iron, aluminum, calcium, and magnesium were removed in the usual way and the mixed alkali chlorids were extracted with amyl alcohol and the extracted residue converted into sulphates. *No. 1* was 250 cc of the laboratory distilled water. *No. 2* was 250 cc of a mineral water at hand in the laboratory containing chiefly calcium sulphate with small amounts of sodium and potassium and a very small amount of lithium. *No. 3* was 250 cc of the same water as *No. 2* to which was added 0.0028 mg of lithium as sulphate. *No. 4* was 250 cc of the same water as *No. 2* with 0.0056 mg of lithium as sulphate added.

The usual procedure in making a complete analysis was carried out and the sulphates of lithium, sodium, and potassium were dissolved in definite quantities of water. The ordinary chemicals in use in the laboratory were employed in the various separations. It was known that these chemicals are frequently contaminated with very small quantities of lithium; in fact, it has been necessary to reject samples of calcium oxid and barium hydroxid which were found to contain excessive amounts of lithium. Where the lithium is present, however, in only very minute traces, it is generally better to use definite amounts of chemicals in making the various separations, always running a blank along with the unknowns and subtracting the corrections obtained in the blank, rather than to attempt to obtain chemicals which are entirely free from such minute amounts of lithium as can be detected by the spectroscope.

<sup>1</sup> Chem. News, 1876, 34: 122.

<sup>2</sup> Gaz. chim. ital., 1906, 36 (II): 855-60.



A standard solution of lithium sulphate was made containing 0.000113 mg per cubic centimeter of lithium. This standard solution was added a little at a time to small quantities of distilled water which was known to be free from lithium, and the resulting solution tested. With 15 cc of water and 1 cc and 2 cc of the above standard lithium solution, the red lithium line ( $\text{Li}_\alpha$ ) failed to appear in two trials. With 15 cc of water and 3 cc of the standard solution, the line appeared strongly once, moderately twice, was doubtful once, and failed to appear twice. This was taken for the limit of concentration and was equivalent to 0.000019 mg of lithium per cubic centimeter. This determination was checked by taking a larger quantity of water, namely 25 cc, to which was added small amounts of the standard lithium solution, a spectroscopic observation being made after each addition. When to the 25 cc of water had been added 5.5 cc of the standard solution, the red line was again just visible, which indicated that the limit was again reached. This corresponded to 0.000020 mg per cubic centimeter. The limit was checked a third time, using 45 cc of water with gradual additions of the standard lithium solution, when it was found that the line faintly appeared when 9 cc had been added, making the limit equivalent to 0.000019 mg per cubic centimeter. The average of the three determinations showed the limit to be for the particular conditions under which the experiments were conducted, 0.000019 mg per cubic centimeter.

It is desirable always to make an observation of the limit at the beginning and at the end of each series of determinations. Samples 1 and 2 were made up to a volume of 10 cc and 5 cc of the solution diluted until the lithium line just disappeared. No. 1 showed the line with 5 cc of the solution plus 15 cc of water. When the water was increased to 20 cc, the line could no longer be detected. Five cubic centimeters of No. 2 showed the line when 35 cc of water were added, but not when 40 cc were added. In the case of No. 1, therefore, when the original 10 cc had been increased in volume to 40 cc, the concentration of the lithium was the same as in the standard solution when the lithium line could barely be seen. The total amount of lithium present, therefore, was 40 times the amount in 1 cc of the diluted standard solution, that is, 40 multiplied by 0.000019, equivalent to 0.0008 mg of lithium. This is the blank and represents the amount of lithium obtained from the reagents used in making the separations. Using the same methods of dilution, No. 2 was found to contain 0.0016 mg. In the examination of these two samples, the dilution method was used rather than the addition of the unknown solution to a definite quantity of water until the appearance of the lithium line, which is the regular method.

The residues from Nos. 3 and 4 were dissolved in water and made up to 100 cc each, and designated as solutions 3 and 4, respectively.

The examination of these solutions was not made on the same day with Nos. 1 and 2, hence a new determination of the observable limit was made. Using the method as described before, the limit at this time was found to be 0.0000168 mg of lithium instead of the 0.000019 found on the previous day. The determination was made by adding to 17 cc of distilled water, portions of solution 3, 1 cc or 0.5 cc at a time, the mixtures being examined after each addition. When 9 cc of solution 3 had been added, the lithium line was observed very faintly once in five trials, showing that the limit had very nearly been reached. When 9.5 cc had been added, the line appeared three times in four trials, which was regarded as the limit. Therefore it will be seen that  $17 + 9.5 = 26.5$  cubic centimeters, each of which contained the equivalent of the observed limit, that is, 0.0000168 mg of lithium or 0.0004452 mg in 9.5 cc of solution 3. Hence, 1 cc of solution 3 contained 0.000047 mg of lithium or the 100 cc, the whole amount, contained 0.0047. When the blank which is equivalent to the amount found in No. 2, 0.0016 mg, is subtracted from the amount found in No. 3, there remains 0.0031 instead of 0.0028 mg of lithium known to have been added to the original sample. In the case of solution 4, 10 cc of distilled water were taken and 3 cc of the solution added. Observation of this mixture gave the line faintly twice out of five trials. When 3.5 cc were added, the line was seen in each of the three trials, from which it will be seen that  $10 + 3.5 = 13.5$  cubic centimeters each of which contained the observed limit of 0.0000168 mg of lithium. The value of the 13.5 cc was therefore 0.000227 mg, which is equivalent to the amount in 3.5 cc of solution 4. One cubic centimeter of solution 4 is therefore equivalent to 0.000065 mg and the total 100 cc contained 0.0065 mg. When the blank determination in No. 2 which is equivalent to 0.0016 is subtracted from the above figure, there remains 0.0049 mg instead of the 0.0056 mg known to have been added. These results are shown in the following tables:

*Determination of lithium added to mineral water (combined amyl alcohol and spectroscopic method).*

Number of solution.	Volume of solution of sulphates.	Used when lithium line was barely visible.			Lithium per cc to barely show lithium line.	Lithium used in test.	Lithium per cc of sulphate solution.	Total lithium in sulphate solution.	Lithium found in mineral water samples; blank subtracted.	Added lithium found.	Amount of lithium added.
		Sulphate solution.	Water.	Total.							
A	B	C	D	$C \times D = E$	$\frac{E}{B} = F$	A × F					
1	cc 10	cc 5	cc 15	cc 20	mg 0.000019	mg 0.0004	mg 0.00008	mg 0.0008	mg	mg	mg
2	10	5	35	40	.000019	.0008	.00016	.0016	0.0008	-----	-----
3	100	9.5	17	26.5	.0000168	.000445	.000047	.0047	.0039	0.0031	0.0028
4	100	3.5	10	13.5	.0000168	.000227	.000065	.0065	.0057	.0049	.0056

While in work of this character it would have been better to have used chemicals which were entirely free from even the most minute traces of lithium, it may be well to add that blanks should always be made and that in this case the blank obtained of 0.0008 mg is the largest blank determination ever found in any of the authors' work. From the above data it will be seen that 250 cc of the original mineral water after subtracting the blank contained 0.0008 mg of lithium or 0.003 mg per liter. Several determinations of the lithium in two liters of other samples of the same water gave figures of less than 0.005 mg of lithium per liter. The use of the combined amyl alcohol and spectroscopic method on some samples of soil gave the following results on the air-dried soils.

*Results on air-dried soils from the use of combined amyl alcohol and spectroscopic method.*

Number and weight of soil.	Total lithium.	Lithium.	Lithium oxid.
<i>Grams.</i>	<i>mg</i>	<i>Per cent.</i>	<i>Per cent.</i>
No. 1:			
10	0.15	0.0015	0.0032
5	.08	.0016	.0034
No. 2:			
10	{ .12	.0012	.0026
	{ .14	.0014	.0030
15	{ .07	.0014	.0030
	{ .08	.0016	.0034
No. 3:			
5	.08	.0016	.0034
15	{ .07	.0014	.0030
	{ .08	.0016	.0034
0.1	.0015	.0015	.0032

<sup>1</sup> Two determinations by the spectroscope of the amount of lithium in the same sample.

As a regular practice in analytical work, the approximate determination of lithium in the mixed chlorids obtained in water analyses saves very much time by indicating whether it is worth while to extract the lithium for weighing. A similar test is regularly made on the solution in nitric acid of the oxids of the calcium and strontium. By making the solution to a definite volume it is easy to tell whether there is enough strontium present to separate and weigh. Though potassium is regularly determined in all complete analyses of water in the Bureau of Chemistry, it is occasionally desired to obtain a close approximation of the amount present in some substance where the information is not worth the trouble and expense of a gravimetric determination. In many of these cases relatively large percentage errors are of no consequence. It is often, however, very desirable to be able to say that there is present 0.001 mg or 0.03 mg rather than report each amount as "trace" or "spectroscopic trace," which may be done if the lines are seen in the spectroscope without any idea as to the amount of the material required to



produce the line. With the Krüss spectroscopic apparatus regularly employed, using a Bunsen burner, the following figures were obtained:

*Results obtained with spectroscope, using a Bunsen burner.*

Metal.	Amount necessary to give spectrum (mg per cc).	Metal.	Amount necessary to give spectrum (mg per cc).
Lithium.....	0.00002	Calcium.....	0.01
Rubidium.....	.03	Strontium.....	.03
Cæsium.....	.01	Barium.....	.05
Potassium.....	.005		

### SUMMARY.

1. In this paper are considered various quantitative methods of separating lithium from the other metals. Some of them have been tested in the Bureau of Chemistry and the method of Gooch,<sup>1</sup> modified slightly in some details of manipulation, has proven entirely satisfactory, when weighable amounts are present.

2. Satisfactory results are obtained by the spectroscopic estimation of lithium according to the methods of Ballmann,<sup>2</sup> Bell,<sup>3</sup> or Foehr,<sup>4</sup> when modified by applying them to the alkalis extracted with amyl alcohol by the Gooch method.

3. Contrary to the statement of Ranzoli<sup>5</sup> the quantitative spectroscopic method is not found preferable to the Gooch method for weighable amounts of lithium.

4. Approximate spectroscopic determinations regularly made of quantities of lithium, potassium, barium, strontium, and calcium are very often of great service as a guide to the proper procedure in analyses.

<sup>1</sup> Amer. Chem. J., 1887, 9; 33-51.

<sup>2</sup> Zts. anal. Chem., 1875, 14; 297.

<sup>3</sup> Amer. Chem. J., 1885, 7; 35.

<sup>4</sup> Chem. Ztg., 1885, 9; 1013.

<sup>5</sup> Gáz. chim. ital., 1901, 31 (I): 40.

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